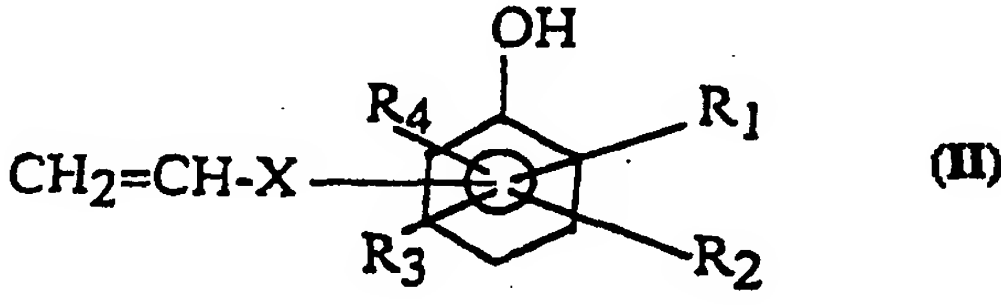


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<p>(21) International Application Number: PCT/FI95/00196 (22) International Filing Date: 10 April 1995 (10.04.95) (30) Priority Data: 941662 11 April 1994 (11.04.94) FI (71) Applicant (for all designated States except US): BOREALIS HOLDING A/S [DK/DK]; Lyngby Hovedgade 96, DK-2800 Lyngby (DK). (72) Inventors; and (75) Inventors/Applicants (for US only): WILEN, Carl-Eric [FI/FI]; Västerlånggatan 29 A 8, FIN-20100 Åbo (FI). NÄSMAN, Jan [FI/FI]; Rakuunatie 58 C 48, FIN-20720 Turku (FI). (74) Agent: BERGGREN OY AB; P.O. Box 16, FIN-00101 Helsinki (FI).</p>		<p>(81) Designated States: CA, JP, NO, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report. In English translation (filed in Finnish).</i></p>
<p>(54) Title: PROCESS FOR THE PREPARATION OF A STABLE α-OLEFIN COPOLYMER</p> <p>(57) Abstract</p> <p>In the invention, a new, stable α-olefin copolymer is produced by causing an α-olefin according to the formula (I): $\text{CH}_2=\text{CRR}'$, where R and R' are, independently of each other, hydrogen or a C₁-C₁₀ alkyl, to react with a copolymer-stabilizing comonomer according to formula (II) where X is a carbon-carbon bond between vinyl carbon and benzene carbon or a C₁-C₂₀ hydrocarbon bridge and R₁, R₂, R₃ and R₄ are hydrogen and/or C₁-C₂₀ hydrocarbon substituents in the benzene ring, in the presence of a π-cyclopentadienyl transition metal compound and an alumoxane compound serving as catalysts.</p> <div style="text-align: right;">  </div>		

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Process for the preparation of a stable α -olefin copolymer

The invention relates to a process for the preparation of a stable α -olefin copolymer, wherein α -olefin is caused to react with a comonomer which stabilizes the copolymer. The invention also relates to an α -olefin copolymer which comprises, as the monomer units, repeating units (mers) of the α -olefin and repeating units (mers) of a comonomer stabilizing the copolymer. Furthermore, the invention relates to a process for the preparation of a copolymer-stabilizing comonomer of the above type and to the use of a phenol resembling the said copolymer-stabilizing comonomer as an activator in the polymerization of α -olefins.

For the polymerization of α -olefins, commonly a Ziegler-Natta catalyst system is used which consists of a so-called procatalyst and a cocatalyst. The procatalyst is based on a compound of a transition metal belonging to any of groups 4-8 of the Periodic Table of the Elements (IUPAC), and the cocatalyst is based on a compound of a metal belonging to any of groups 1(A)-8(A) of the Periodic Table of the Elements (IUPAC). A separate group among the procatalysts is formed by metallocene-type transition-metal compounds, i.e. compounds in which one unsaturated ring or several, such as a cyclopentadienyl ring, is bonded to the transition metal with a π -bond.

US patent publication 3 242 099 discloses a catalyst system intended for the polymerization of α -olefins, in which system bis-cyclopentadienyl titanium dichloride is combined with an oligomeric alumoxane compound.

US patent publication 4 404 344 discloses a process for the preparation of homopolymers and copolymers of ethylene and propylene by the polymerization of one or several monomers by means of a catalyst system formed by bis-cyclopentadienyl zir-

conium dimethyl and a lower alkyl alumoxane. The publication states that ethylene can be copolymerized with propylene, 1-butene, 1-hexene or α,ω -dienes.

EP-69 952 and US-4 542 199 describe the polymerization of C_1 - C_{10} olefins in the presence of a catalyst system which is made up of bis-cyclopentadienyl zirconium dichloride or bis-cyclopentadienyl zirconium monomethylmonochloride and linear or cyclic methylalumoxane.

From, for example, the publication "Catalytic Olefin Polymerisation", eds. Keii, T., Soga, K., Kodansha, Tokyo and Elsevier, Amsterdam, 1990, 439-534, there is known the use of chiral ansa-metallocenes, such as $Et(Ind)_2ZrCl_2$ and $Me_2Si(IndH_4)_2ZrCl_2$, i.e. metallocenes containing cyclopentadienyl compounds bridged to each other, for isospecific, syndiospecific, anisotactic and hemi-isotactic polymerization.

Most commercial polymers, and in particular polypropylene, decompose under environmental effects, for example under the effects of heat, heat and oxygen, and radiation, throughout their existence, for example, during machining, storage and use. To prevent this decomposition, stabilizers, anti-oxidants and UV stabilizers and protectors are usually mixed with a polymer.

It is typical of high-yield catalysts to have an ability to give to the forming polymer the particle form of the original catalyst, which is replicated from polymer particles having a diameter of 0.2-5 mm. The forming polymer particles are, however, porous and are therefore easily oxidized. It is indeed the general practice that the polymer obtained from the reactor is caused to melt and stabilizers are added to it, whereafter the product is granulated.

The melt-mixing with stabilizers after the preparation of the

polymer, and the subsequent granulation, could be eliminated if the stabilization were performed during the polymerization step. In this case the product of the polymerization would as such be ready for onward processing. Owing to stabilization problems, it has not been possible in the case of polymer products to exploit fully a process for preparing a particulate product.

During use, stabilizers and other additives may migrate to the surface of products, whereby their stabilizing effect is reduced. Additive losses may be caused by evaporation during melt processing, loss during the washing step, the migration of polar additive components, and uneven distribution of stabilizer additives in the polymer matrix. The last-mentioned is often caused by the incompatibility of stabilizers, due to high polarity, with paraffin-type hydrocarbon-based polymers. In particular, amine stabilizers, such as paraphenyldiamine derivatives, tend to separate from the polyolefin matrix. In addition, the stabilizer amount which can be added to polyolefins is limited, since the additive tends to crystallize.

It is in accordance with the state of the art to use as additives high molar mass stabilizers, such as derivatives of tertiary butylphenol and pentaerythritol. Another state-of-the-art method is to use polymer-based oligomeric molecules. This procedure, however, has a limitation in the simultaneously lowered solubility of the additive in the polymer.

Recently, special attention has been paid to the covalent linking of the stabilizing groups to the molecular frame of the polymers. Thus, DE publication 1 947 590 discloses a method for the preparation of copolymers, wherein α -olefin is caused to react ethylenically with an unsaturated metal phenoxide in the presence of a catalyst made up of a titanium or vanadium halogen compound and an organoaluminum or organozinc compound. The organometal compounds may be omitted if the metal phenoxide has

a metal-carbon bond. DE publication 1 570 541 discloses the copolymerization of propylene with 4-(ω -alkenyl)-N,N-dimethylaniline by using as the catalyst a heterogeneous Ziegler-Natta catalyst which is sensitive to polar stabilizer comonomers.

In polymerization in accordance with this known technology, the polymerization activity has been so low that the processes have remained laboratory curiosities. The polymerizations have namely been performed by means of an old-fashioned catalyst which is based on titanium trichloride or titanium tetrachloride and alkyl and aluminum compounds.

Subsequently the olefin polymerization technology has developed to the present level, in which one gram of catalyst is capable of polymerizing up to 30 kg of α -olefin. The copolymerization of polar components with these high-yield catalysts has not been known on an industrial scale owing to the tendency of these components to form, with the active centers of the catalyst, compounds which inhibit polymerization. Thus, polar components such as alcohols, water and acetone have indeed been used for discontinuing polymerization when the desired molar mass has been reached. Another obstacle is evidently that in polymerization a sterically large-sized stabilizer monomer is not capable of approaching the active centers on the surface of a carrier.

An object of the present invention is to provide a process for the preparation of a stable α -olefin copolymer with a maximal yield. A more detailed object is the copolymerization of α -olefin with a monomer-type stabilizer by using a high-yield catalyst system of a new type. The plan is in this case to prepare, directly in the polymerization step, stabilized polymer particles of a suitable size. A key object is also to provide a usable copolymer the stabilizer component of which will remain evenly distributed in the polymer product without becoming separated as a separate phase. It is also an aim of the

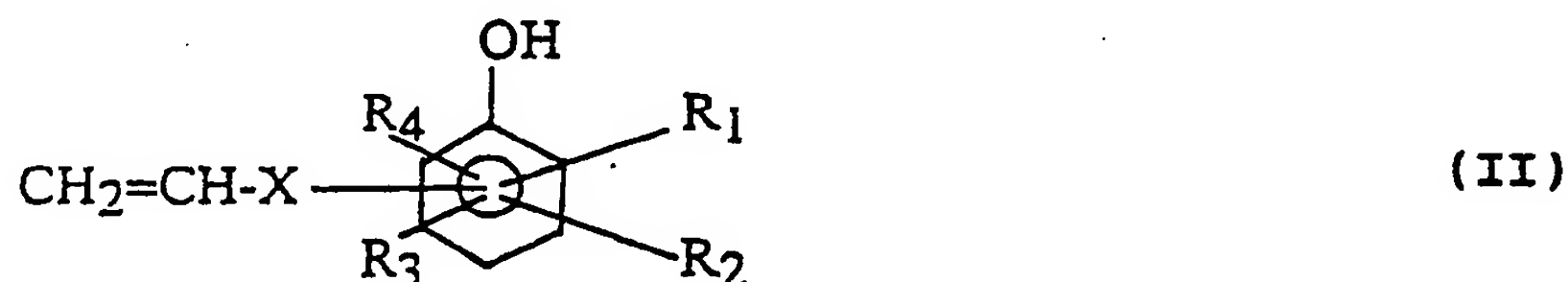
invention to provide a compound or comonomer which stabilizes the copolymer and at the same time has an activating effect on the polymerization.

The above objects have now been achieved by a new process for the preparation of a stable α -olefin copolymer, the process being mainly characterized in what is stated in the characterizing clause of Claim 1.

In the process, α -olefin is caused to react with a comonomer which stabilizes the copolymer, in which case the α -olefin used is an olefin according to Formula (I)



where R and R' are, independently of each other, hydrogen or a C_1 - C_{10} alkyl, and the copolymer-stabilizing comonomer used is a compound according to Formula (II)



where X is a carbon-carbon bond between vinyl carbon and benzene carbon or a C_1 - C_{20} hydrocarbon bridge, preferably a C_6 - C_{12} hydrocarbon bridge, and R_1 , R_2 , R_3 and R_4 are hydrogen substituents and/or C_1 - C_{20} hydrocarbon substituents in the benzene ring, and the catalyst is a π -cyclopentadienyl transition metal compound and an alumoxane compound. To our knowledge, the copolymerization of stabilizer comonomers and α -olefin with a catalyst based on a π -cyclopentadienyl transition metal compound and an alumoxane compound has not been presented previously. It has thus been realized that the polymerization of α -olefin and the copolymer-stabilizing comonomer stated

above works excellently if the catalyst used is a combination of a π -cyclopentadienyl transition metal compound and an alumoxane compound.

The α -olefin usable in the process according to the invention can be any α -olefin copolymerizable with a Ziegler-Natta system. Typical α -olefins of this type are ethylene, propylene, 1-butene, isobutylene and 4-methyl-1-pentene. The α -olefin according to Formula (I) used in the process according to the invention may also be a mixture which contains polymerizable α -olefins of various types. Furthermore, monomers other than monomers according to Formulae (I) and (II) may also participate in the polymerization of the process according to the invention. Since polypropylene is, with respect to its commercial importance, relatively unstable and easily oxidizable, the invention is especially usable if the α -olefin according to Formula (I) is propylene.

In the process according to the invention, an α -olefin according to Formula (I) is thus caused to react with a copolymer-stabilizing comonomer according to Formula (II). As stated above, it is a prerequisite for the functioning of a Ziegler-Natta system, which the π -cyclopentadienyl transition metal compound/alumoxane compound used in the present invention is also deemed to be, that the copolymer-stabilizing comonomer must not, with its reactive hetero group, poison the catalyst. Although the substituents in the benzene ring of the comonomer according to Formula (II) may be quite freely distributed, it is, however, preferable if in the comonomer at least one, and preferably two, of the group which includes the bridge X and substituents R_1 , R_2 , R_3 and R_4 , is a secondary, most preferably tertiary, alkyl which is in the ortho-position relative to the hydroxyl group. It is also preferable that, in the said comonomer, the bridge X, which is a C_1 - C_{20} hydrocarbon bridge, is attached in the ortho- or para-position of the benzene ring, in which case R_1 is preferably a branch C_3 - C_6 alkyl and is at-

tached in the ortho-position of the benzene ring, and at least two of groups R_2 , R_3 and R_4 are hydrogen. In this case the hydroxyl of the benzene ring is flanked by at least one, and preferably two, alkyl substituents, and preferably a branched alkyl substituent. It is especially preferable if the copolymer-stabilizing comonomer according to Formula (II) is 6-tert.-butyl-(2-(1,1-dimethylhept-6-enyl))-4-methylphenol.

One key idea of the invention is that an α -olefin is copolymerized with a copolymer-stabilizing comonomer in the presence of a catalyst which is based on a π -cyclopentadienyl transition metal compound and an alumoxane compound.

By a π -cyclopentadienyl transition metal compound is meant in this context a catalytically active transition metal compound in which the transition metal has at least one cyclopentadienyl ligand bonded with a π bond. Such a ligand is very stable, and it can be deemed to form a six-electron aromatic anion $C_5H_5^-$. Owing to its aromatic stability it may also be substituted, especially in such a manner that it is fused with another ring. These compounds are also called metallocenes. According to one embodiment, the π -cyclopentadienyl transition metal compound has the following general formula (III)



where Cp is an unsubstituted, substituted or fused π -cyclopentadienyl, R^5 is an organic group, Y is a halogen, and m is an integer 1-3, n is an integer 0-3, and o is an integer 0-3. It is preferable if the π -cyclopentadienyl transition metal compound is a compound or derivative of two π -cyclopentadienyl ligands and a group 4 transition metal, such as bis- π -cyclopentadienyl titanium(IV) derivative, bis- π -cyclopentadienyl zirconium(IV) derivative, or bis- π -cyclopentadienyl hafnium(IV) derivative, preferably a bridged bis-indenyl zirconium(IV) derivative or a bridged bis-indenyl hafnium(IV) derivative. In

the last-mentioned case, by bridged is meant that both of the indenyl ligands are bound to each other by a chemical group such as ethylene or silylene, in which case the ethylene or silylene bridge is attached to the six-carbon-atom ring of the indenyl group. By indenyl derivative is also meant that the indenyl may be fully aromatic or the six-carbon-atom fusion ring may be aliphatic, i.e. it may contain four hydrogen atoms (IndH_4).

It is especially preferable if the π -cyclopentadienyl transition metal compound used in the process and serving as a catalyst is $(\text{CH}_3)_2\text{Si}(\text{IndH}_4)_2\text{ZrCl}_2$ or $(\text{C}_2\text{H}_4)(\text{IndH}_4)_2\text{ZrCl}_2$, preferably racemic $\text{rac.}(\text{CH}_3)_2\text{Si}(\text{IndH}_4)_2\text{ZrCl}_2$, where IndH_4 stands for a tetrahydroindenyl group, see above. These preferred π -cyclopentadienyl transition metal compounds have been discussed in, for example, EP patent application 344 887 A3, which is incorporated herein by reference.

Although the π -cyclopentadienyl transition metal compounds which we deem to be the most preferable have been stated above, it is also possible to use other analogous compounds. Such compounds have been listed, for example, in EP application 303 519 from page 3, line 59 to page 4, line 31 and in EP application 260 999 on page 4, lines 14-30. Both publications are hereby incorporated in the present application by reference.

The other catalyst component in the polymerization process according to the invention is an alumoxane compound. It preferably has the following general formula (IV)



or



where R^6 stands for an organic group and p is an integer 1-50. Formula (IVa) applies when the alumoxane compound is ring-like by structure and Formula (IVb) applies when the structure of the alumoxane compound is linear.

Group R^6 in the alumoxane compound according to Formula (IV) is preferably a lower alkyl group having 1-5 carbon atoms, and most preferably methyl. p in the formula is preferably such that alumoxane is at least an oligomer, and it is preferably an integer 4-20.

The alumoxane used in the invention can be prepared in many ways, for example by contacting water with trialkylaluminum or by contacting trialkylaluminum with hydrogenated salt, such as hydrogenated copper sulfate or iron sulfate. When the aim is to prepare at least oligomers of alumoxane, the alumoxane is preferably prepared with the aid of hydrogenated iron(IV) sulfate or hydrogenated copper sulfate. In this case the dilute solution of trialkylaluminum in toluene, benzene or xylene is treated with $FeSO_4 \cdot 7H_2O$ or $CuSO_4 \cdot 5H_2O$. The molar ratio of hydrogenated sulfate to trialkyl aluminum is in general 1:5 - 1:10, and the reaction temperature is within the range $-40^\circ C$ - $+60^\circ C$, in which case methane gas is released in the reaction. Usually the product obtained consists of both linear and ring-like alumoxane having an oligomerization degree of 6 or higher when the reaction is a success.

The molar ratio between the metals of the alumoxane compound and the π -cyclopentadienyl transition metal compound used as a catalyst in the polymerization process according to the invention may vary widely. The general rule is that aluminum is used in a considerably larger amount than is the transition metal compound. According to one embodiment the said molar ratio between the metals is within the range 100,000:1 - 10:1, preferably 10,000:1 - 1000:1, and most preferably approx. 5000:1 -

1000:1.

The catalyst system used in the process according to the invention may be either homogenous or heterogenous. In a heterogenous system, a carrier can be used both for the π -cyclopentadienyl transition metal compound and for the alumoxane compound, or a π -cyclopentadienyl transition metal compound and a carrier treated, for example impregnated, with an alumoxane compound can be added to the polymerization mixture. Suitable carriers include silica, alumina, magnesia, zirconia, magnesium silicate, alkylated silicates, and certain polymers, such as granular polyethylene. It is, however, preferable to use in the present invention a carrier-free catalyst system of a π -cyclopentadienyl transition metal compound and an alumoxane compound, the polymerization and catalysis being preferably carried out in a hydrocarbon solvent, such as toluene.

Although the catalyst system used in the process according to the invention is based on a π -cyclopentadienyl transition metal compound and an alumoxane compound, it may also contain other catalytic components and catalyst auxiliaries. These include other transition-metal compounds and aluminum compounds and possibly electron donors.

The polymerization is typically carried out by feeding into an inert polymerization reactor a copolymer-stabilizing comonomer, a π -cyclopentadienyl transition metal compound, an alumoxane, a solvent, and a gaseous α -olefin to start polymerization. From the viewpoint of the invention the order in which the various components are added is not critical. A typical polymerization process is slurry polymerization.

Typically an autoclave, flushed with dry and oxygen-free nitrogen, is filled with a solvent, such as toluene, whereafter the first portion of the solution of alumoxane in the solvent is added, Simultaneously the π -cyclopentadienyl transition metal

compound is added to the second portion of the alumoxane solution, whereafter this second portion is also fed into the reactor. At this stage, α -olefin may be fed into the reactor, possibly by using pressure, to initiate the polymerization with only α -olefin, i.e. to achieve so-called prepolymerization.

After suitable prepolymerization, a copolymer-stabilizing comonomer may be added, which has been suitably dissolved in the solvent used in the polymerization. The feeding in of the stabilizer comonomer may be done, for example, by means of pressurized α -olefin, such as propylene. During the polymerization proper, the rate of α -olefin is maintained constant, for example by adjusting the reaction pressure. After a suitable time, polymerization is discontinued by removing, when necessary, any unreacted α -olefin and by adding a catalyst poison, such as alcohol. Finally the obtained stable α -olefin copolymer is separated, washed and dried.

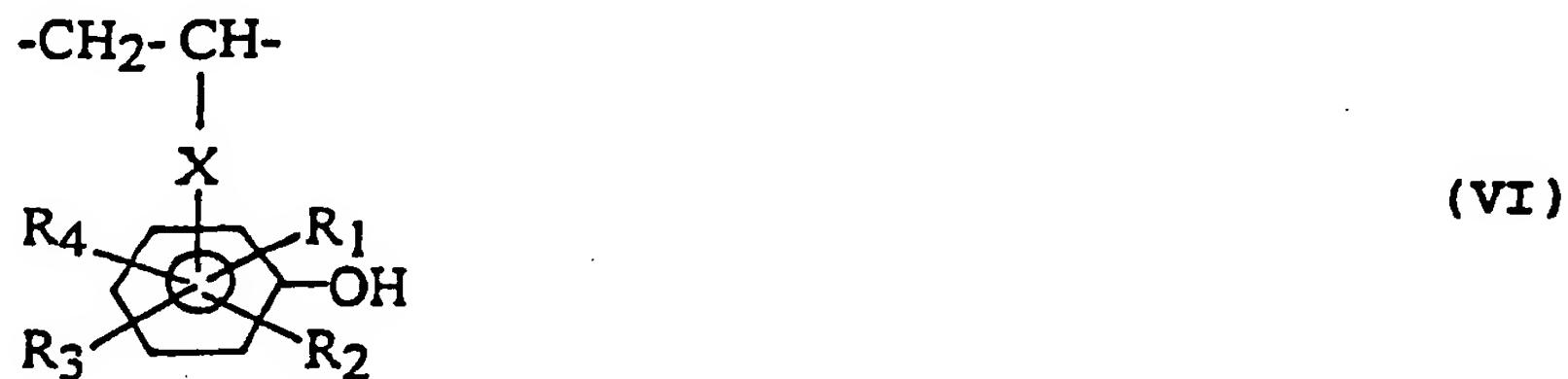
In the process according to the invention for the preparation of a stable α -olefin copolymer it is preferable if the α -olefin is caused to react with the copolymer-stabilizing monomer at a temperature of 5-50 °C, preferably 10-30 °C, and most preferably 15-25 °C. A suitable reaction time is approx. 10-120 min, preferably approx. 20-80 min. In the invention it is also preferable if the molar ratio Al/comonomer, preferably Al/6-tert.-butyl(2-(1,1-dimethylhept-6-enyl))-4-methylphenol is adjusted to a value of 3-10, preferably to a value of 4-8. At the same time it is preferable, the α -olefin being gaseous at NTP and being preferably propylene, to adjust the partial pressure of α -olefin in the reaction to 1-5 bar.

Although the invention has focussed on the copolymerization of only one α -olefin and one copolymer-stabilizing comonomer, it is evident from the viewpoint of the idea of the invention that it is also possible to use a plurality of copolymer-stabilizing comonomers.

In addition to the process, the invention also relates to a stable α -olefin copolymer which comprises, as monomer units, repeating units (mers) of an α -olefin and repeating units (mers) of a copolymer-stabilizing comonomer. The α -olefin copolymer according to the invention is mainly characterized in what is stated in the characterizing clause of Claim 16. It has thus been realized that an α -olefin copolymer is easy to prepare and that it is stable if it is made up of α -olefin units, which are in accordance with the following formula (V)



where R and R' are, independently of each other, hydrogen or a C_1 - C_{10} alkyl, and that the repeating unit of the copolymer-stabilizing comonomer is in accordance with Formula (VI)



where X is a carbon-carbon bond between vinylene carbon and benzene carbon or a C_1 - C_{20} hydrocarbon bridge, preferably a C_6 - C_{12} hydrocarbon bridge, and R_1 , R_2 , R_3 and R_4 are hydrogen substituents and/or C_1 - C_{20} hydrocarbon substituents in the benzene ring.

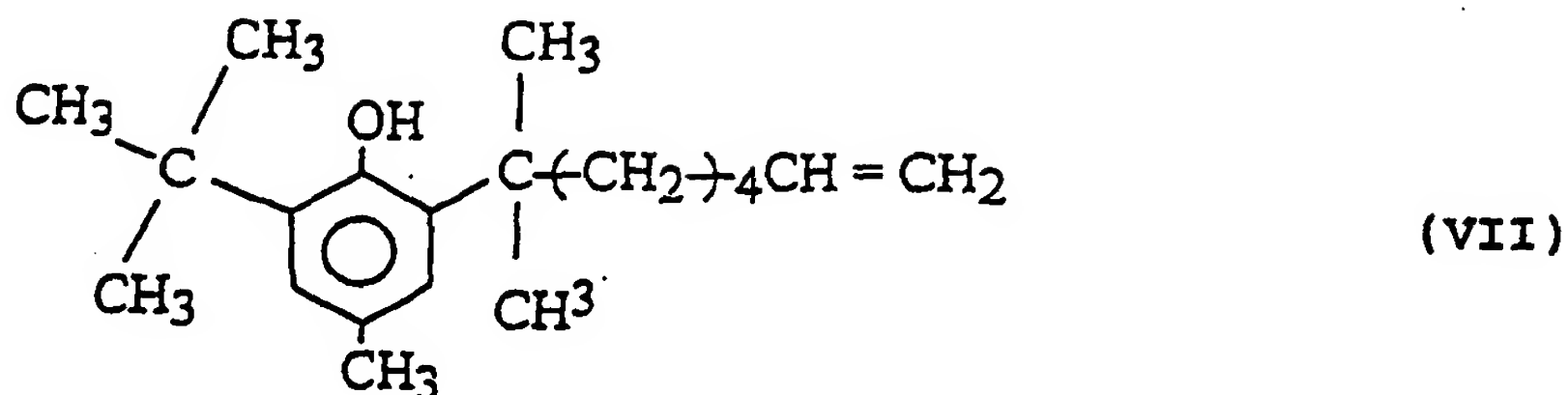
An α -olefin copolymer according to the invention may contain α -olefin units of one or more types, such as a unit of ethylene, propylene, 1-butene, isobutylene or 4-methyl-1-pentene. It is especially preferable if, in the α -olefin repeating unit according to Formula (V), R is methyl, i.e. the repeating unit is a propylene unit. The α -olefin copolymer may also contain a plurality of repeating units according to Formula (V) and addi-

tionally other comonomer units.

According to one preferred embodiment, in the repeating unit according Formula (VI) of a copolymer-stabilizing monomer, at least one, and preferably two, of bridges X and substituents R_1 , R_2 , R_3 , and R_4 is a secondary, preferably tertiary, alkylene or alkyl, which is in the ortho-position with respect to the hydroxyl group.

It is preferable if in the repeating unit according to Formula (VI) of the copolymer-stabilizing comonomer the bridge X is attached in the ortho- or para-position of the benzene ring, R_1 is a branched C_3 - C_6 alkyl and attached in the ortho-position in the benzene ring, and at least two of the groups R_2 , R_3 and R_4 are hydrogen. We also refer to the structure of the copolymer-stabilizing comonomer, discussed above in connection with the process, and to the advantages related thereto. It is especially preferable if the repeating unit, in accordance with Formula (VI), of the copolymer-stabilizing comonomer is a 6-tert.-butyl-(2-(1,1-dimethylhept-6-enylenyl))-4-methylphenol unit. In the preparation of the α -olefin copolymer according to the invention it was observed that the molar mass distribution was considerably narrow, which suggests that the catalyst has active centers of only one type. The molar mass distribution measured as a ratio of polydispersity, i.e. weight-average molar mass, to the number-average molar mass, M_w/M_n , is preferably below 4, and most preferably approx. 1.5-2.5.

The stable α -olefin copolymer according to the invention and the process for the preparation thereof are also closely associated with a process for the preparation of a comonomer which stabilizes the copolymer and crucially activates the polymerization. The invention thus also relates to a process for the preparation of the most preferred copolymer-stabilizing comonomer, i.e. 6-tert.-butyl-(2-(1,1-dimethylhept-6-enyl))-4-methylphenol. This compound has the formula (VII)

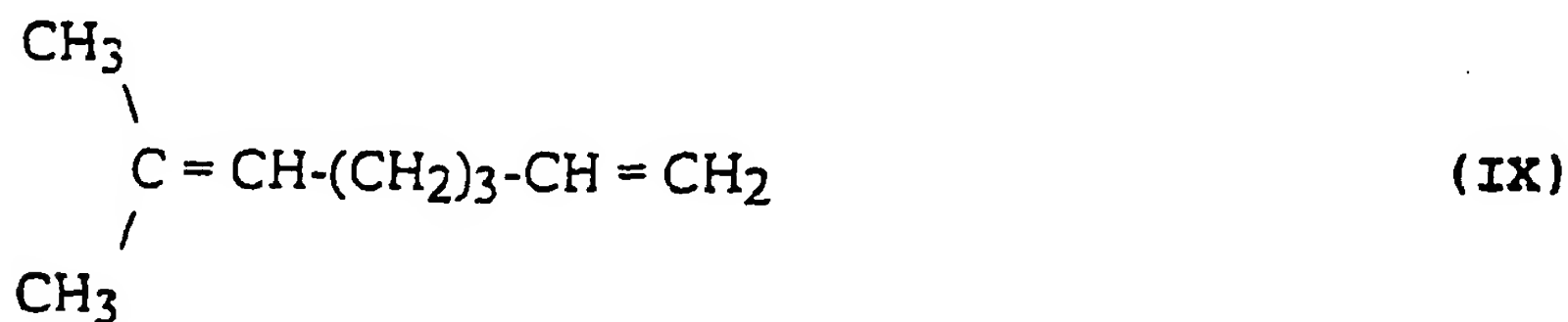


The process for the preparation of this comonomer is characterized in that 6-tert.-butyl-4-methylphenol (VIII)



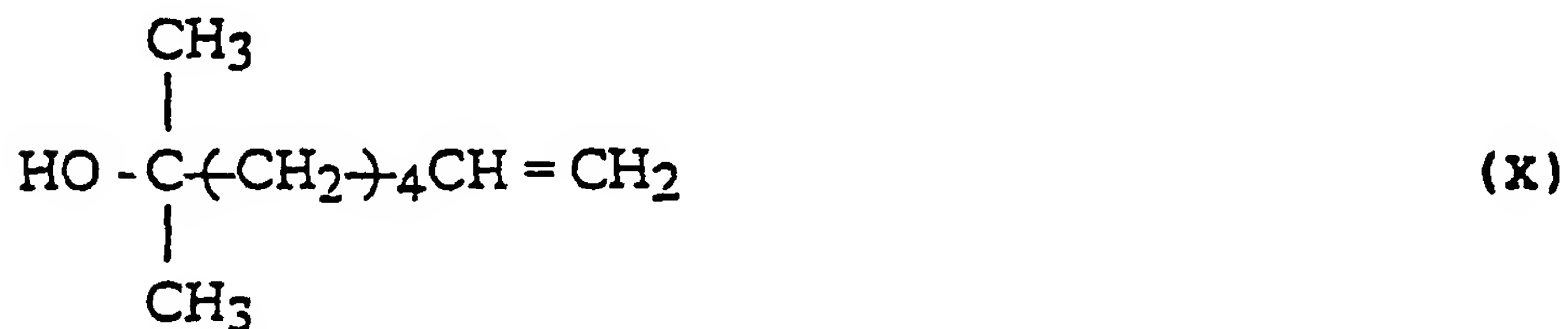
is caused to react under acid conditions with either

- a) 7-methyl-1,6-octadiene (IX)



or

- b) 7-methyl-oct-1-ene-7-ol (X)

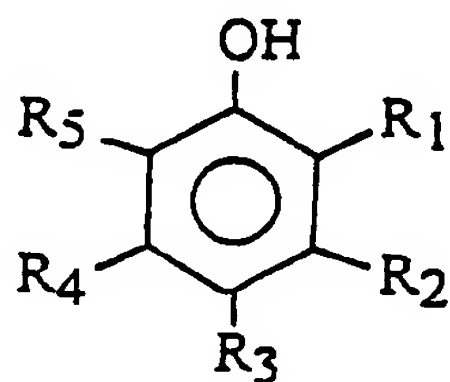


whereafter the formed reaction mixture is neutralized and the product (VII) is recovered therefrom.

Process a) is typically carried out by mixing the components and heating them to, for example, 50-100 °C, and by thereafter adding to the mixture an acid catalyst, such as sulfuric acid. Thereafter the mixture is allowed to react for 24 hours, whereafter neutralization and extraction by means of a suitable solvent, such as hexane, are carried out. Finally separation, for example by distillation, is performed.

In process b) the components are mixed together, heated, and treated with an acid catalyst in quite the same manner as in process a). After an approximately equally long reaction time, neutralization, extraction, and separation, for example by distillation, are carried out.

In the research of the polymerization process according to the invention it was observed, surprisingly, that the copolymer-stabilizing phenol monomer according to Formula (II) strongly activated copolymerization between itself and an α -olefin. The reaction velocity increased up to 10-fold. In the same connection it was observed that this strongly activating effect was not limited only to a phenol monomer but applied to all substituted phenols. Such activating effect of a substituted phenol on the copolymerization of α -olefin when a π -cyclopentadienyl transition metal compound and an alumoxane are used as the catalyst has not been previously observed or taught. Thus the invention relates, according to one viewpoint, to the use of a compound according to Formula (XI)



(XI)

where R_1 , R_2 , R_3 , R_4 , and R_5 are hydrogen or a C_1 - C_{20} hydrocarbon, in which case at least two of the R-groups are C_1 - C_{20}

hydrocarbons, as an activator in α -olefin polymerization where in the catalyst used consists of a π -cyclopentadienyl transition metal compound and an alumoxane. The preferred embodiments are in the main the same parameters as were stated above in connection with the polymerization process according to the invention.

A number of examples are presented below, their only purpose being to illustrate the invention.

Examples

Materials

All of the chemicals which were used for the preparation of 6-tert.-butyl-(2-(1,1-dimethylhept-6-enyl))-4-methylphenol and $\text{rac.}-(\text{CH}_3)_2\text{Si}(\text{IndH}_4)_2\text{ZrCl}_2$ were reaction pure and prepared by Aldrich. The $\text{rac.}-(\text{CH}_3)_2\text{Si}(\text{IndH}_4)_2\text{ZrCl}_2$ was prepared substantially in accordance with EP patent 344 887. The 6-tert.-butyl-(2-(1,1-dimethylhept-6-enyl))-4-methylphenol was prepared substantially by an acid-catalyzed reaction between 2-tert.-butyl-4-methylphenol and 7-methyl-1,7-octadiene, which will be described below. The following chemicals were used in the copolymerization experiments: high-purity propylene (Neste Oy, Finland, 99.5 %) and nitrogen (AGA, Finland, 99.9999 %), high-purity toluene (refluxed in the presence of CaH_2 and thereafter distilled in an argon atmosphere), methylalumoxane (a 30 wt.% toluene solution of MAO, Scheering, the MAO containing trimethylaluminum TMA in an amount of approx. 25 % by weight).

Polymerization

The sample-taking from the π -cyclopentadienyl transition metal compound and alumoxane and from the phenolic monomer took place in a nitrogen atmosphere which contained oxygen less than 2 ppm and water less than 5 ppm. The reaction temperature was c n-

trolled within ± 0.3 °C by using a Lauda circulating bath. The slurry polymerizations were conducted in a 0.5 l jacketed autoclave equipped with a blade turbine stirrer. The dry glass autoclave was evacuated and flushed with nitrogen. This was repeated several times. Thereafter the first portion, i.e. 200 ml of freshly distilled toluene, was fed into the autoclave by means of nitrogen overpressure in order to reduce any impurities in the reactor. At the same time the ansa-metallocene (5 mg) was dissolved in the second portion, i.e. the MAO/toluene solution, and was preactivated by allowing it to stand at room temperature for 5 min. Thereafter the catalyst/-activator mixture was fed into the reactor. The prepolymerization was started by adding only propylene monomer ($P_{\text{propylene}} = 1.4$ bar). After 5 minutes, a suitable amount of a phenolic stabilizer comonomer diluted in 15 ml of toluene was introduced into the reactor by means of gaseous propylene until the partial pressure of propylene reached 2 bar. The polymerization rate was determined by measuring the rate of propylene consumption, the total pressure in the reactor remaining constant as gaseous propylene was added continuously. After 60 min, the polymerizations were quenched by removing the propylene rapidly and by adding 100 ml of methanol. The produced polyolefin was filtered and the catalyst residues were removed by a treatment with a 1 % methanol/HCl solution. Thereafter the polyolefin was washed twice with ethanol, was dried under vacuum at 50 °C, and was weighed for the determination of the polymerization yield. The copolymer was extracted by refluxing with 2-propanol/cyclohexane for 24 h in a Soxhlet apparatus before the concentration of bound phenolic stabilizer comonomer was determined and thermo-oxidative tests were conducted.

Properties of the polymer

The proportion of bound phenolic stabilizer was determined by UV analysis, and the numeric values are based on polypropylene-/Irganox 1076 standards. The UV spectra were obtained by using

a Shimadzu UV-240 spectrometer. The spectra were recorded between 220 and 350 nm. The phenolic stabilizer comonomer had a strong absorbance in this region at the wavelength 280 nm, and all of the measurements were performed at this wavelength. The melting and crystallization thermograms were recorded by a Perkin-Elmer DSC IV system, the temperature being increased from 50 °C to 200 °C at a rate of 10 °C/min. The sweeping gas used was nitrogen. The results of the second scan were reported in order to eliminate differences in sample history. Crystallinity was determined from the DSC curves by using a fusion heat of 49.8 cal/g. The thermo-oxidative stability of the extracted copolymers was investigated by means of oven aging, where the sample was at a temperature of 110 °C and in air, whereafter the oxidation products were detected by means of a Perkin-Elmer 1710-IR spectrometer. The increase of the absorbance peak at wave number 1720 cm^{-1} is associated with products of hydrocarbon oxidation, such as acids, aldehydes and ketones. The formation time of the carbonyl peak was recorded. ^{13}C NMR analyses were carried out with a Jeol 400 MHz spectrophotometer at 110 °C. The polymer samples were dissolved in 1,1,2,2-tetrachloroethane- d_2 . The GVC chromatograms were obtained with a Waters model 150 C at 135 °C, the polymer samples being dissolved in 1,2,4-trichlorobenzene.

Results of copolymerization

Copolymerizations of propylene and 6-tert.-butyl-(2-(1,1-dimethylhept-6-enyl))-4-methylphenol in accordance with Scheme I were carried out by varying the concentrations of the monomers in relation to each other, the results obtained being shown in Table I. In addition, copolymerizations were carried out by varying the ratio Al/Zr while all of the other parameters remained constant, and the results of these copolymerizations are depicted graphically in Figure 1.

The polymerization activity increased considerably when the

molar ratio Al/phenol exceeded the value 4.4, whereafter the activity decreased gradually as the molar ratio Al/phenol decreased. The molar masses of the copolymers increased as the concentration of the phenolic stabilizer comonomer increased, and the molar mass of copolymer produced using high concentrations corresponded to the molar mass of a polypropylene prepared under the same conditions, and therefore it is unlikely that the stabilizing phenolic comonomer served as a chain transfer agent. The molar mass distributions of the copolymers were in general within the range 1.9-2.1, which corresponds to the typical polymerization results of a catalyst which contains active centers of one type. A comparison with a homopolymer showed that the crystallinities and melting points of the copolymers were lower, as expected. With lower polymerization temperatures the molar masses increased while the molar mass distribution remained almost constant, while the melting points increased from 126 °C to 150 °C and the polymer activity decreased in the manner shown in Table II when the temperature was lowered from 20 °C to -20 °C.

The ^{13}C NMR spectra showed that the phenolic stabilizer comonomer became copolymerized with propylene by means of the $\text{rac.}-(\text{CH}_3)_2\text{Si}(\text{IndH}_4)_2\text{ZrCl}_2/\text{MAO}$ system which served as a catalyst.

In Figure 4, the FT-IR spectrum (b) of the extracted copolymer is compared with polypropylene (a) prepared using the same catalyst. This spectrum, also, shows that what is in question is a copolymer of propylene and the phenolic stabilizer monomer.

The thermo-oxidative stability of the copolymer was determined in an oven at 110 °C in the presence of air. The results were determined by the above-mentioned FT-IR analysis. The results are shown in Table III. Before the copolymers were kept in the oven they were extracted by refluxing for 24 hours in a Soxhlet

apparatus by using 2-propanol/cyclohexan as the extraction liquid, to remove any monomer residues. With the copolymers shown in Table III, a carbonyl peak appeared at 400-700 hours at 110 °C, whereas unstabilized polypropylene had a strong carbonyl peak already at 6 hours.

Kinetic profiles of homo- and copolymerizations

The polymerization rates of the formation of homo- and copolymers, expressed in terms of $R_p = \text{kg polymer} / \text{g catalyst} \cdot \text{h}$ are directly dependent on the feed rate of propylene into the semibatch reactor operated at constant pressure and temperature. The kinetic profiles for the polymerizations after the adding of the phenolic stabilizer monomer before the adding of the metallocene catalyst, and 5, 20 and 40 min after the starting of the propylene polymerization are graphically plotted in Figure 5. Propylene homopolymerization had a steady-state kinetic curve, whereas copolymerizations showed a decay-type kinetic behavior. The decrease in catalytic activity during copolymerization can be explained by a reduction, as a function of the polymerization time, of the strongly activating effect of the phenolic stabilizer, since approx. 60 % of the phenolic stabilizer monomer originally fed is incorporated into the copolymer within 20 min. That the polymerization rate increased from the initial value of 5 kg polymer / g catalyst · h to 28 kg polymer / g catalyst · h when polar 6-tert.-butyl-(2-(1,1-dimethylhept-6-enyl))-4-methylphenol was added has been neither described nor suggested previously.

Since the phenolic comonomer used thus accelerated polymerization catalyzed by a π -cyclopentadienyl transition metal compound and an alumoxane compound, a non-monomeric substituted phenol was added to the polymerization mixture by way of experimentation. When 2,6-di-tert.-butylphenol was added to the mixture, and propylene homopolymerization was carried out, the results graphically plotted in Figure 6 were obtained. Also,

when 2,6-di-tert.-butylphenol (0.0344 mol/l) was added 5 min after the starting of propylene polymerization, a similar increase in the initial polymerization rate of propylene occurred. The polymerization rate of propylene increased almost 8-fold after a short induction time, and polymerization was brought to completion within as few as 30 minutes. This result confirms that a phenolic monomer and, more widely, a substituted phenol, activates the active centers of the catalyst system used in the present invention.

Tabl 1

Results of the copolymerization of propylene and 6-tert.-butyl-(2-(1,1-dimethylhept-6-enyl))-4-methylphenol

Ex.	C _{phenol} ^{b)} mol/l	Al/phenol molar ratio	Activity kg polym./ g cat. h	M _n g/mol	P _d ^{c)}	Crys. d) %	M.P. °C	Concentration of bound stabilizer % by weight
1	0	-	5.0	28000	1.9	43	146	0
2	0.0172	7.4	12.6	10000	2.1	29	130	1.3
3	0.0264	5.2	12.3	10000	2.1	30	126	2.5
4	0.0344	4.4	9.6	14000	2.1	33	128	3.8
5	0.0472	3.0	1.5	35000	1.9	33	138	5.5

- a) Polymerization conditions:
catalyst: rac.-(CH₃)₂Si(IndH₄)₂ZrCl₂, cocatalyst: MAO, Al/Zr = 3000, P_{propylene} = 2 bar, polymerization time 60 min, T = 20 °C, and V_{toluene} = 250 ml. A suitable amount of phenolic stabilizer monomer was added at 5 min after the starting of the propylene polymerization.
- b) S_{phenol} stands for the concentration of 6-tert.-butyl-(2-(1,1-dimethylhept-6-enyl))-4-methylphenol.
- c) P_d stands for molar mass distribution, i.e. polydispersity, see p. 13.
- d) Crys. stands for polymer crystallinity, which was determined from the DSC curves, the melting temperature of a folded-chain polypropylene crystal being assumed to be 49.8 cal/g.
- e) The bound phenolic stabilizer amount was determined by UV spectrometry after the copolymer had been extracted for 24 hours by refluxing with a 50:50 solution of 2-propanol and cyclohexane.

Table II

Effect of the polymerization temperature on the molar mass and on catalyst activity ^{a)}

Ex.	C _{phenol} mol/l	Temp. °C	Activity kg polym./ g cat. h	M _n g/mol	M _w g/mol	P _d	T _m °C
1	0	20	5.0	28000	52000	1.9	146
2	0.0264	20	12.3	10000	21000	2.1	126
6	0.0264	0	0.7	64000	121000	1.9	146
7	0.0264	-20	0.03	132000	249000	1.9	150

a) Polymerization conditions: Al/Zr = 3000, C_{propylene} = 1.5 mol/l, V_{toluene} = 250 ml, and polymerization time = 60 min. The phenolic stabilizer was added at 5 min after the starting of the propylene polymerization.

Table III

Thermo-oxidative stability results of extracted copolymers by using FTIR spectrometry after the samples had been stored in air and a temperature of 110 °C

Ex.	Concentration of bound stabilizer % by weight	M _n ^{c)} g/mol	P _d ^{d)}	Time of formation of carbonyl peak h
8	-	28000	1.9	6
9	3.7 ^{b)} (80 %)	20000	2.1	700
10	3.8 (80 %)	14000	2.1	600
11	3.1 (94 %)	14000	2.5	700
12	2.8 (62 %)	10000	2.5	400

a) These polymers were prepared by processes a-e illu-

strated in Figure 5, i.e. the polymerization was done according to process a, etc.

- b) (%) stands for the conversion of the phenolic monomer to copolymer, i.e. (%) = [(copolymerized phenolic monomer / phenolic monomer originally fed in) · 100 %].
- c) Number-average molar mass was measured before extraction.
- d) Polydispersity was measured before extraction.

Scheme I

Copolymerization of propylene and 6-tert.-butyl-(2-(1,1-dimethylhept-6-enyl))-4-methylphenol

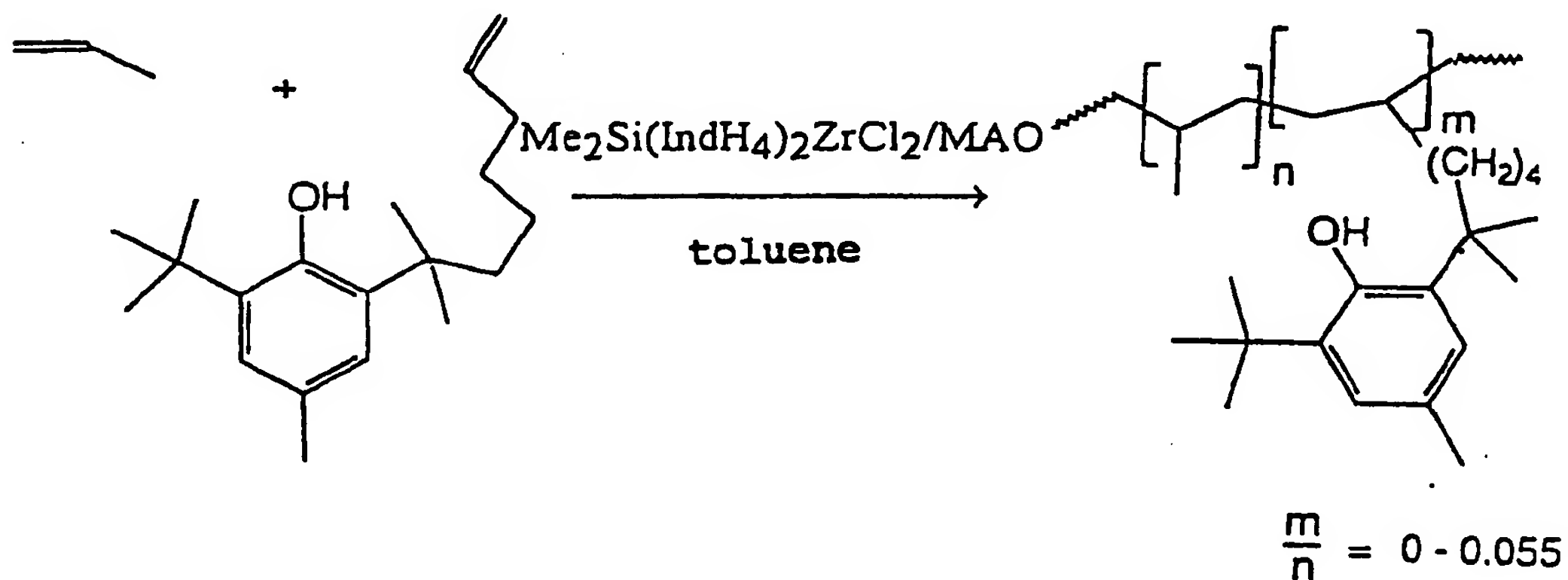


Figure 1

Activities of the polymerization of propylene and the copolymerization of propylene and 2-tert.-butyl-(2(1,1-dimethylhept-6-enyl))-4-methylphenol (0.0344 mol/l) at various Al/Zr molar ratios, the catalyst used being $(\text{CH}_3)_2\text{Si}(\text{IndH}_4)_2\text{ZrCl}_2/\text{MAO}$ and the concentration of the Zr compound being maintained constant at $0.044 \cdot 10^{-3}$ mol/l. The polymerization conditions were as follows: $T = 20^\circ\text{C}$, $t_p = 60$ min, $V_{\text{toluene}} = 250$ ml, and $P_{\text{propylene}} = 2$ bar. a) = propylene homopolymerizations. b) copolymerization of propylene and 2-tert.-butyl-(2(1,1-dimethylhept-6-enyl))-4-methylphenol. The phenolic stabilizer was added at 5 min after the starting of the propylene polymerization.

Figure 2

^{13}C NMR spectrum of polypropylene (1,1,2,2-tetrachloroethane- d_2 as the solvent).

Figure 3

^{13}C NMR spectrum of the copolymer (1,1,2,2-tetrachloroethane- d_2 as the solvent).

Figure 4

a) = FTIR spectrum of polypropylene. b) FTIR spectrum of copolymer.

Figure 5

Velocity profiles of the polymerization of propylene and the copolymerization of 2-tert.-butyl-(2-(1,1-dimethylhept-6-enyl))-4-methylphenol, the comonomer being added at different times and the catalyst used being $(\text{CH}_3)_2\text{Si}(\text{IndH}_4)_2\text{ZrCl}_2/\text{MAO}$. The polymerization conditions were: Al/Zr = 3000, $T = 20^\circ\text{C}$, $P_{\text{propylene}} = 2$ bar, and $V_{\text{toluene}} = 250$ ml. a) = propylene polymerization. b) phenolic stabilizer (final concentration 0.0344 mol/l) was first precomplexed with MAO for 75 min before the adding of the metallocene catalyst. The non-precomplexed

phenolic monomer (same final concentration) was added at c) 5 minutes, d) 20 minutes, and e) 40 minutes after the starting of the propylene polymerization.

Figure 6

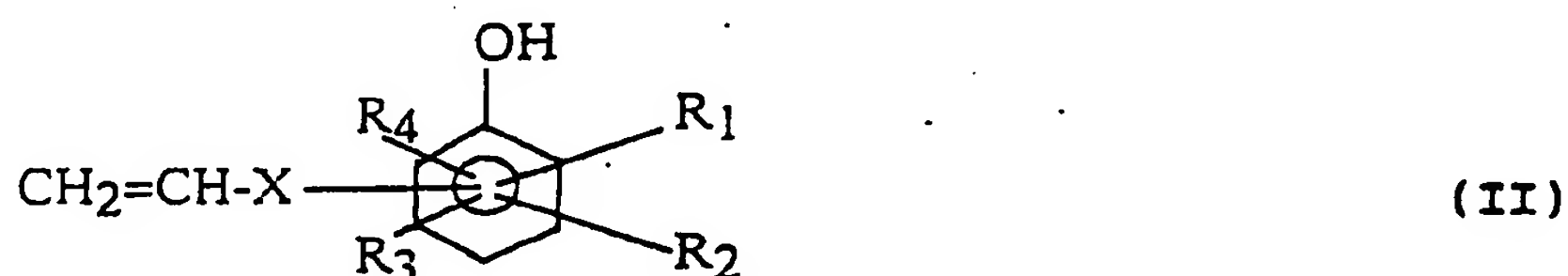
Velocity profiles of propylene polymerization with and without phenol, the catalyst used being $(\text{CH}_3)_2\text{Si}(\text{IndH}_4)_2\text{ZrCl}_2/\text{MAO}$. Polymerization conditions: $\text{Al/Zr} = 3000$, $T = 20^\circ\text{C}$, $P_{\text{propylene}} = 2$ bar, and $V_{\text{toluene}} = 250$ ml. a) 2,6-di-tert.-butylphenol (0.0344 mol/l) was added at 5 min after the starting of the propylene polymerization. b) homopolymerization of propylene.

Claims

1. Process for the preparation of a stable α -olefin copolymer, wherein an α -olefin is caused to react with a comonomer which stabilizes the copolymer, characterized in that an α -olefin according to Formula (I)



where R and R' are, independently of each other, hydrogen or a C_1 - C_{10} alkyl, is caused to react with a copolymer-stabilizing comonomer according to Formula (II)



where X is a carbon-carbon bond between vinyl carbon and benzene carbon or a C_1 - C_{20} hydrocarbon bridge, preferably a C_6 - C_{12} hydrocarbon bridge, and R_1 , R_2 , R_3 , and R_4 are hydrogen and/or C_1 - C_{20} hydrocarbon substituents in the benzene ring, in the presence of a π -cyclopentadienyl transition metal compound and an alumoxane compound serving as catalysts.

2. A process according to Claim 1, characterized in that in the α -olefin according to Formula (I) R is methyl and R' is hydrogen, i.e. the α -olefin is propylene.

3. A process according to Claim 1 or 2, characterized in that in the copolymer-stabilizing comonomer according to Formula (II) at least one, and preferably two, of the bridges X and of substituents R_1 , R_2 , R_3 and R_4 is a secondary, most preferably tertiary, alkyl, which is in the ortho-position relative to the hydroxyl group.

4. A process according to Claim 1, 2 or 3, characterized in that in the copolymer-stabilizing comonomer according to Formula (II) the bridge X is attached in the ortho- or para-position in the benzene ring, R_1 is a branched C_3 - C_6 alkyl and is attached in the ortho-position in the benzene ring, and at least two of the groups R_2 , R_3 and R_4 are hydrogen.

5. A process according to Claim 4, characterized in that the copolymer-stabilizing comonomer according to Formula (II) is 6-tert.-butyl-(2-(1,1-dimethylhept-6-enyl))-4-methylphenol.

6. A process according to any of the above claims, characterized in that the π -cyclopentadienyl transition metal compound serving as a catalyst is a compound according to Formula (III)



where Cp is an unsubstituted, substituted or fused π -cyclopentadienyl, R^5 is an organic group, Y is a halogen, and m is an integer 1-3, n is an integer 0-3, and o is an integer 0-3.

7. A process according to Claim 6, characterized in that the π -cyclopentadienyl transition metal compound is a bis- π -cyclopentadienyl group 4 (IUPAC) transition metal derivative, such as a bis- π -cyclopentadienyl titanium(IV) derivative, a bis- π -cyclopentadienyl zirconium(IV) derivative, or a bis- π -cyclopentadienyl hafnium(IV) derivative, preferably a bridged bis-indenyl zirconium(IV) derivative or a bridged bis-indenyl hafnium(IV) derivative.

8. A process according to Claim 7, characterized in that the π -cyclopentadienyl transition metal compound is $(CH_3)_2Si(IndH_4)_2ZrCl_2$ or $(C_2H_4)(IndH_4)_2ZrCl_2$, preferably racemic rac. $(CH_3)_2Si(IndH_4)_2ZrCl_2$, where $IndH_4$ stands for a tetrahydroindenyl group.

9. A process according to any of the above claims, characterized in that the alumoxane compound serving as a catalyst is a compound according to Formula (IV)



or



where R^6 stands for an organic group and p is an integer 1-50.

10. A process according to Claim 9, characterized in that R^6 is a lower alkyl, preferably methyl.

11. A process according to any of the above claims, characterized in that the α -olefin is caused to react with the copolymer-stabilizing monomer at a temperature of 5-50 °C, preferably 10-30 °C, most preferably 15-25 °C.

12. A process according to any of the above claims, characterized in that the reaction time is set at 10-120 min, preferably 20-80 min.

13. A process according to any of the above claims, characterized in that the atomic ratio Al/transition metal, preferably Al/Zr, is adjusted to 1000-10000, preferably approx. 2000-5000.

14. A process according to any of the above claims, characterized in that the molar ratio Al/comonomer, preferably Al/6-tert.-butyl-(2-(1,1-dimethylhept-6-enyl))-4-methylphenol, is adjusted to 3-10, preferably 4-8.

15. A method according to any of the above claims, characterized in that, the α -olefin being gaseous at NTP, its pressure, and preferably the pressure of propylene, is adjusted to 1-5 bar.

16. An α -olefin copolymer which comprises, as the monomer units, repeating units (mers) of an α -olefin and repeating units (mers) of a copolymer-stabilizing comonomer, characterized in that the repeating unit of α -olefin is in accordance with the following Formula (V)



where R and R' are, independently of each other, hydrogen or a C_1 - C_{10} alkyl, and that the repeating unit of copolymer-stabilizing comonomer is in accordance with the following Formula (VI)



where X is a carbon-carbon bond between vinyl carbon and benzene carbon or a C_1 - C_{20} hydrocarbon bridge, preferably a C_6 - C_{12} hydrocarbon bridge, attached in the ortho-position in the benzene ring, and R_1 is a branched C_3 - C_6 alkyl and is attached in the ortho-position in the benzene ring, and at least two of the groups R_2 , R_3 , R_4 , which may be hydrogen and/or C_1 - C_{20} hydrocarbon substituents in the benzene ring, are hydrogen.

17. An α -olefin copolymer according to Claim 16, characterized in that in the α -olefin repeating unit according to Formula (V) R is methyl and R' is hydrogen, i.e. the repeating unit is a propylene unit.

18. An α -olefin copolymer according to Claim 16 or 17, characterized in that in the repeating unit, according to Formula (VI), of copolymer-stabilizing monomer at least one, and preferably two, of the bridges X and substituents R_1 , R_2 , R_3 and R_4 is a secondary, most preferably tertiary, alkenyl or alkyl, which is in the ortho-position relative to the hydroxyl group.

19. An α -olefin copolymer according to any of Claims 16-18, characterized in that the repeating unit, according to Formula (VI), of copolymer-stabilizing comonomer is a 6-tert.-butyl-(2-(1,1-dimethylhept-6-enylenyl))-4-methylphenol unit.

20. An α -olefin polymer according to any of Claims 16-19, characterized in that its polydispersity, i.e. the ratio of its weight-average molar mass to its number-average molar mass $M_w/M_n < 4$, preferably approx 1.5-2.5.

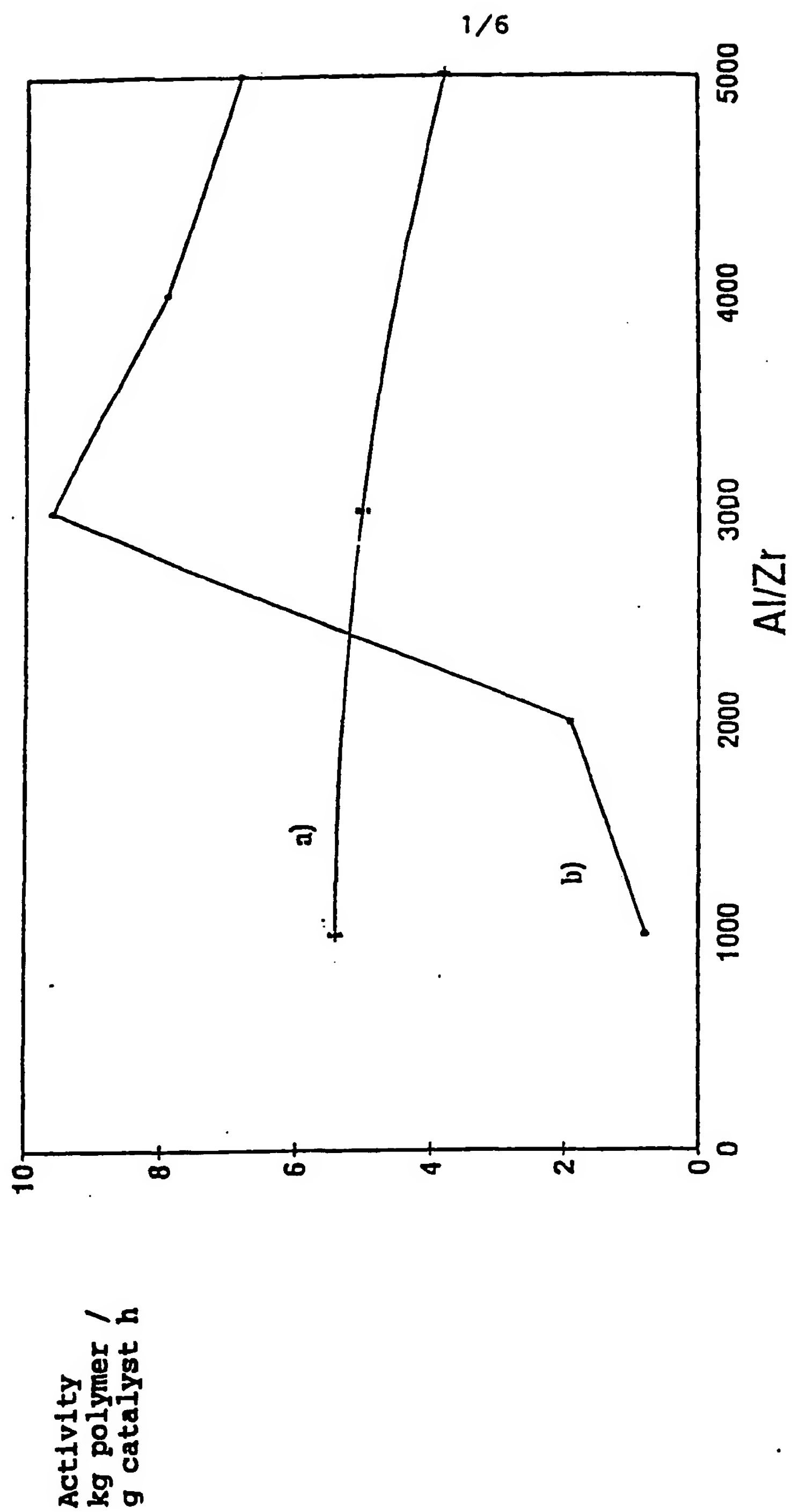


FIG. 1

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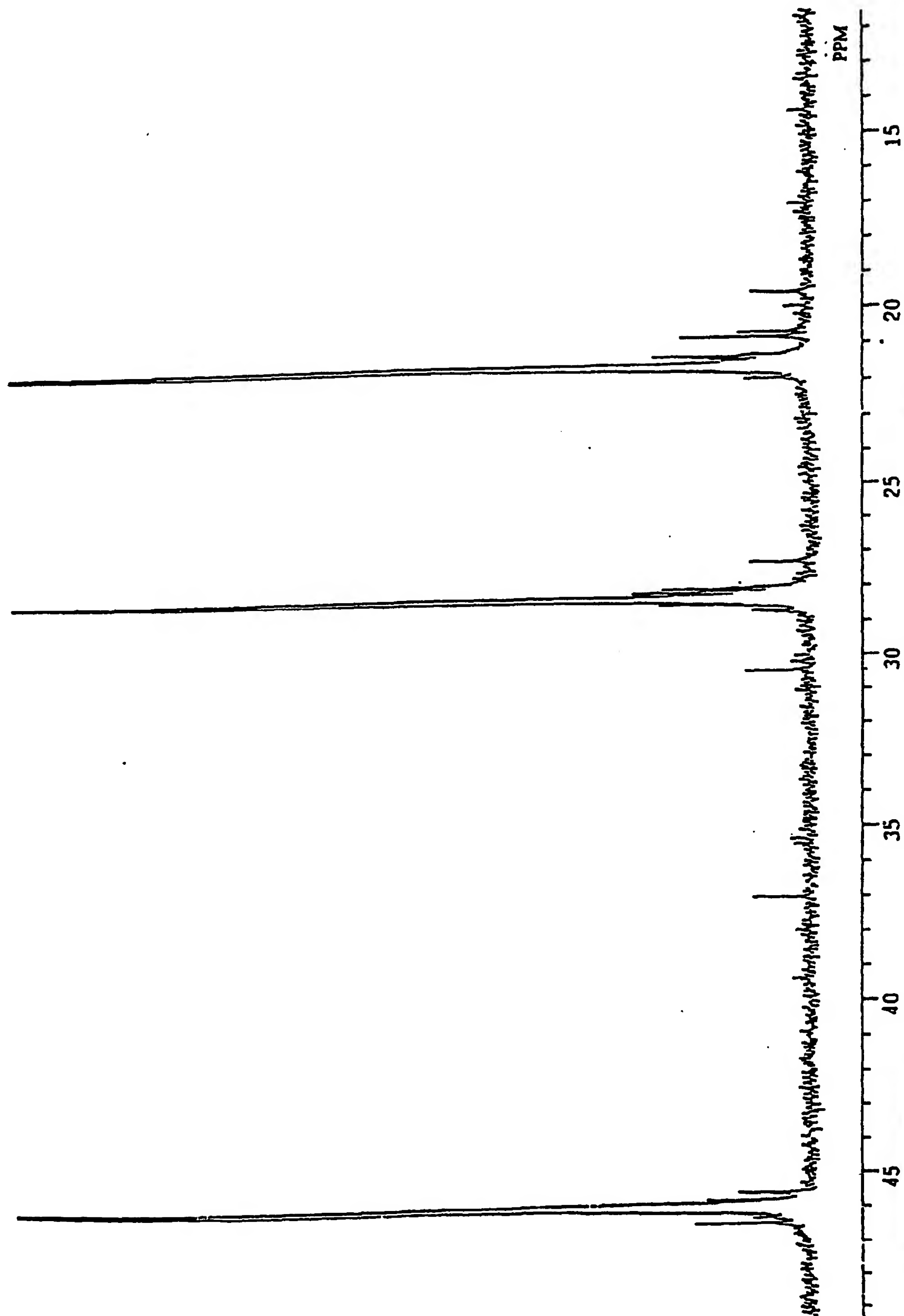


FIG. 2

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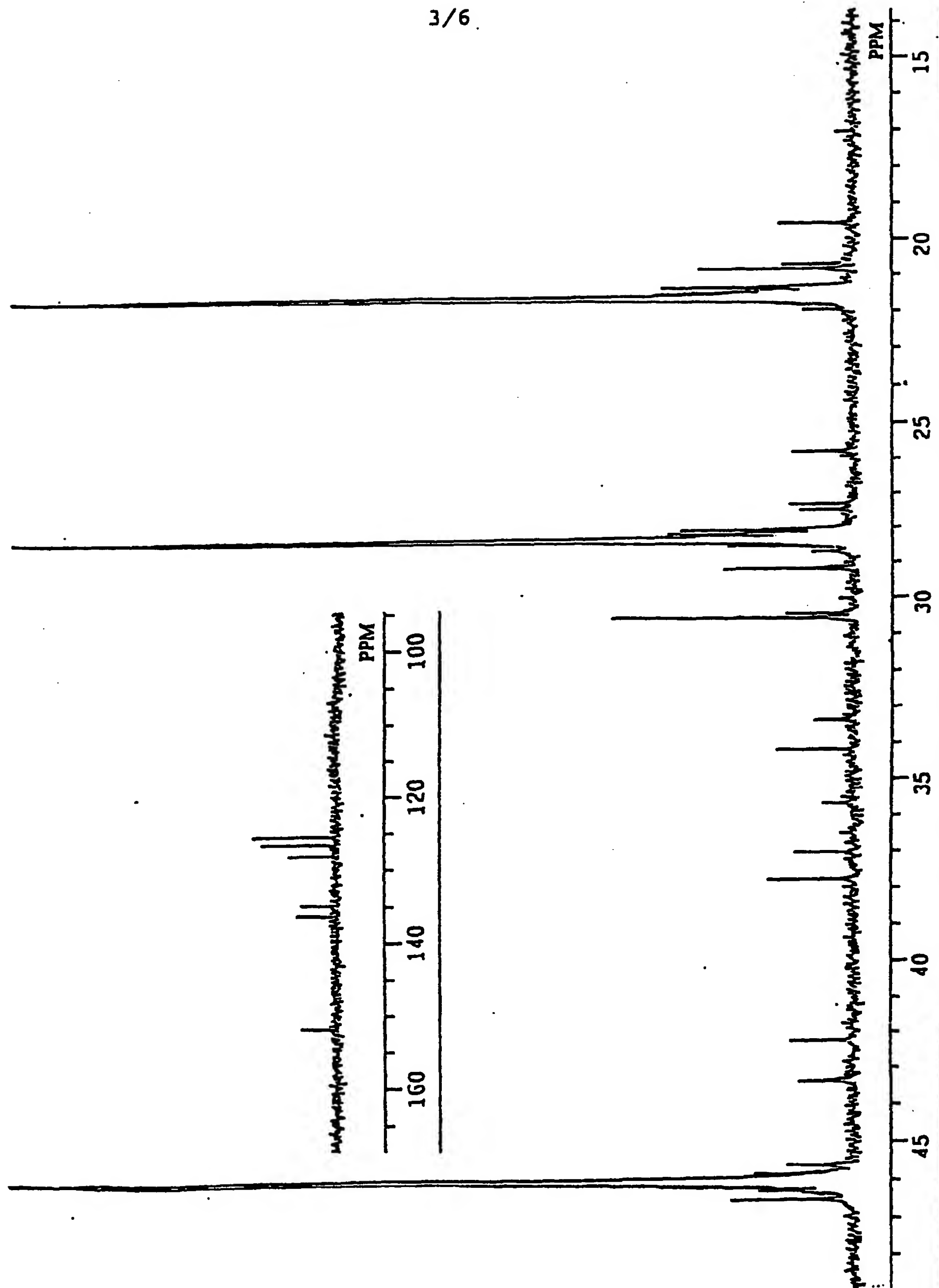


FIG. 3

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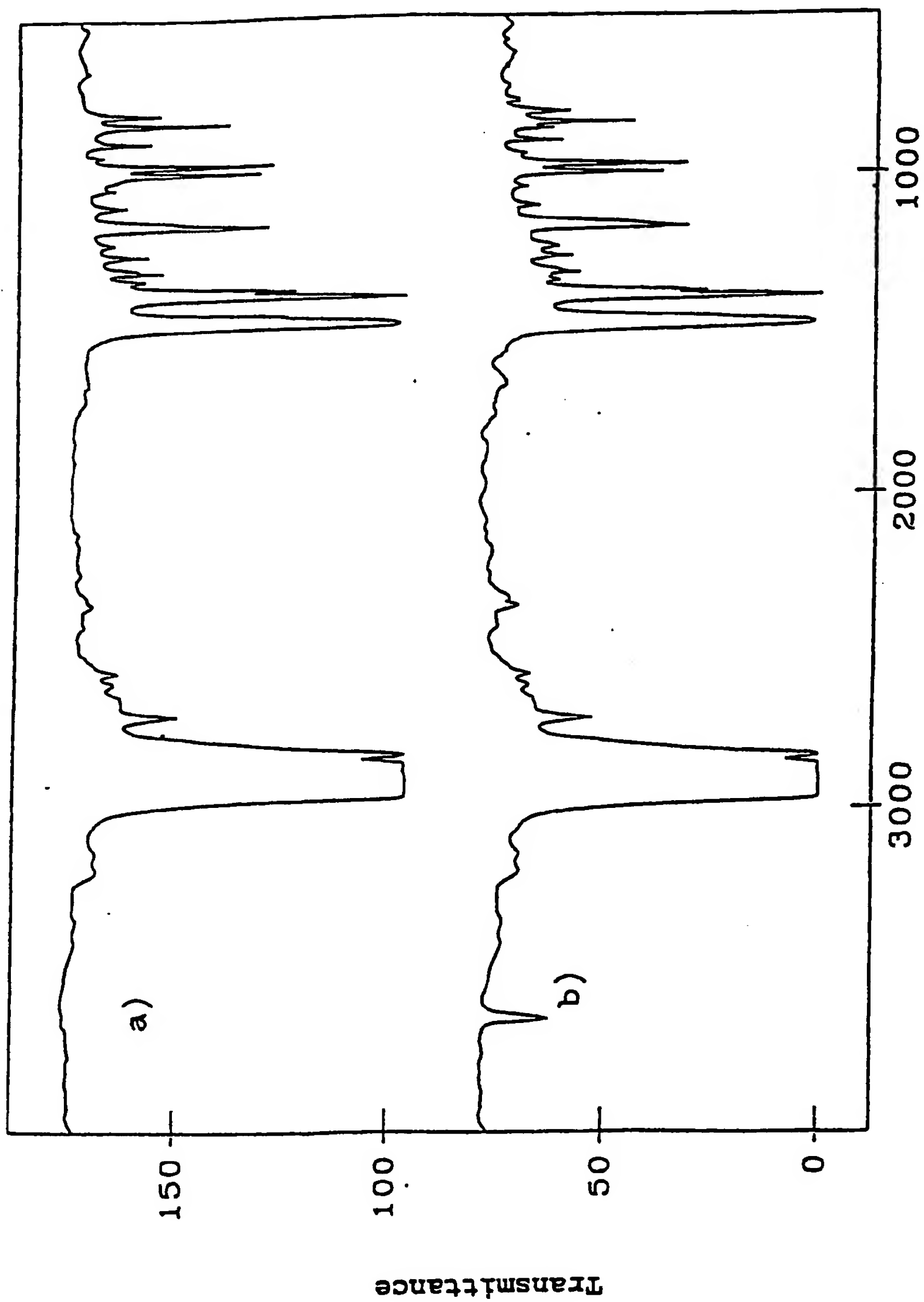


FIG. 4 Wave number (cm - 1)

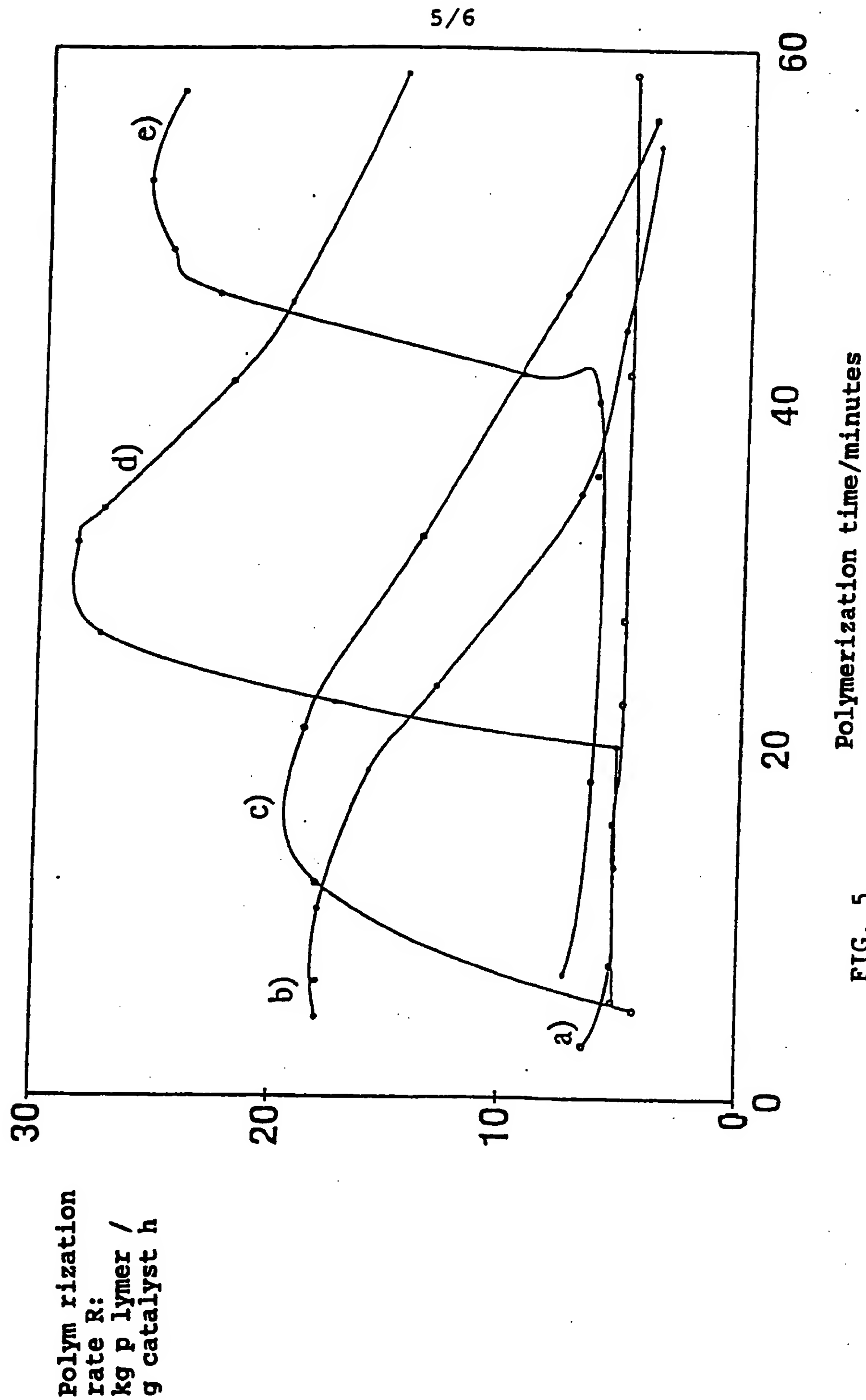


FIG. 5

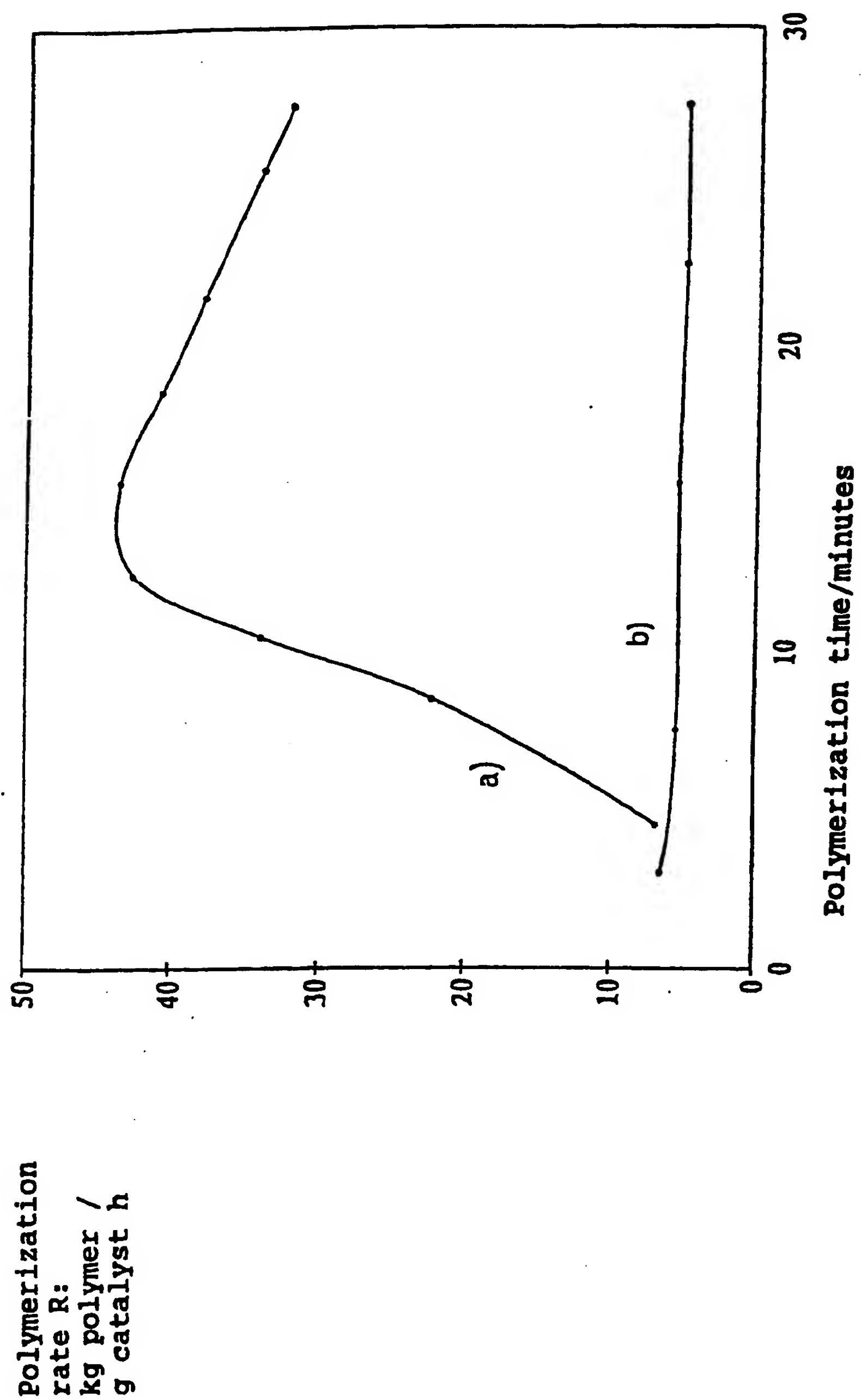


FIG. 6

INTERNATIONAL SEARCH REPORT

International application No.
PCT/FI 95/00196

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C08F 210/00, C08F 4/642

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim N .
X	DE 1917230 A1 (ESSO RESEARCH AND ENGINEERING COMPNAY), 22 January 1970 (22.01.70), examples 7-11 and claim --	1-4, 16-18
X	DE 1947590 B2 (MITSUI PETROCHEMICAL INDUSTRIES LTD), 17 November 1977 (17.11.77), column 7, line 65 - column 8, line 5, claim 2 --	1-4, 16-18
P,X	FI 92212 B (BOREALIS POLYMERS OY), 30 June 1994 (30.06.94), claims 1,5, abstract --	1,3-4, 16, 18

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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Date of the actual completion of the international search

11 July 1995

Date of mailing of the international search report

14 -07- 1995

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 95/00196

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0545140 A1 (BASF AKTIENGESELLSCHAFT), 9 June 1993 (09.06.93), page 5, line 23 - line 42; page 6, line 4 - line 20 -----	1-20

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/FI 95/00196

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE-A1- 1917230	22/01/70	US-A- 3477991	11/11/69
DE-B2- 1947590	17/11/77	FR-A, A- 2018465	29/05/70
		GB-A- 1278516	21/06/72
		NL-A- 6914107	19/03/70
		NL-A- 6914109	19/03/70
FI-B- 92212	30/06/94	NONE	
EP-A1- 0545140	09/06/93	DE-A- 4139261	03/06/93